PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-012583
(43)Date of publication of application : 14.01.1997

(51)Int.Cl. C07F 7/04
C08L 83/02

(21)Application number : 07-157897
(22)Date of filing : 23.06.1995

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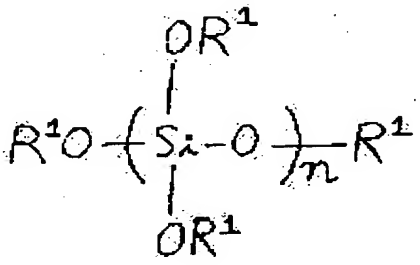
(54) SILOXANE COMPOUND, ITS PRODUCTION AND CURABLE COMPOSITION

(57)Abstract:
PURPOSE: To produce a siloxane compound, represented by a specific rational formula, excellent in compatibility with various components, stability in various solvents, film-forming properties, transparency, resistance to boiling water, etc., of films and useful for curable compositions, etc.
CONSTITUTION: This siloxane compound is a compound represented by the formula SiOa(OH)b(OR1)c(OR2)d [0.8≤a≤1.6; 0.3≤b≤1.3; 0.2≤[c+d]≤1.9; b=4-[2a+c+d]; R1 is methyl or ethyl; R2 is an organic group different from R1]. The compound is obtained by hydrolyzing and condensing a compound of the formula Si(OR1)4, providing an oligomer of the formula [n is 2-8], then adding a compound of the formula R2OH thereto and carrying out the transesterification.

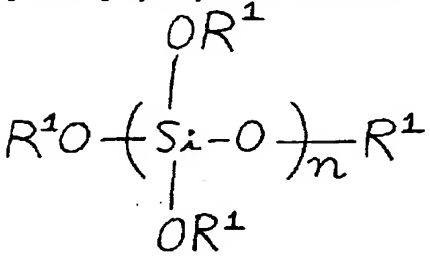


LEGAL STATUS

[Date of request for examination]	31.07.2001
[Date of sending the examiner's decision of rejection]	01.02.2005
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3740714
[Date of registration]	18.11.2005
[Number of appeal against examiner's decision of rejection]	2005-03586
[Date of requesting appeal against examiner's decision of rejection]	02.03.2005
[Date of extinction of right]	

CLAIMS

[Claim(s)]
[Claim 1] The siloxane compound expressed with the following rational formulas.
[Formula 1] SiOa(OH)b(OR1) c(OR2) d (0.8<=a<=1.6, 0.3<=b<=1.3, 0.2 <=c+d<=1.9, b=4- (2 a+c+d), organic radical on which a methyl group or an ethyl group, and R2 are [R1] different from each other with R1)
[Claim 2] The siloxane compound according to claim 1 whose R1 is a methyl group.
[Claim 3] Hydrolysis condensation of the alkoxysilane shown by Si (OR1)4 is carried out, and it is [Formula 2].

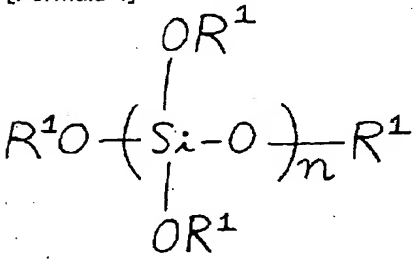


(— however, the manufacture approach of the siloxane compound according to claim 1 or 2 characterized by including the process which n considers as the oligomer expressed with or more 2 eight or less integer), and adds and carries out the ester interchange of the alcohol expressed with R2OH to this.
[Claim 4] The hardenability constituent which comes to blend a siloxane compound according to claim 1 or 2 with this and a compound with compatibility.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to a hardenability constituent at a siloxane compound and its manufacture approach, and a list.
[0002]
[Description of the Prior Art] By introducing a silyl radical into organic resin, the improvement of the degree of hardness of a paint film, acid resistance, etc. is tried conventionally. Furthermore, alkoxysilane, such as a tetra-ethoxy silane, a tetramethoxy silane, methyl trimetoxysilane, ethyltrimethoxysilane, dimethyldimethoxysilane, and vinyltrimetoxysilane, and the oligomer which carried out partial hydrolysis condensation of these are independently used as a coating agent in recent years, or blending these with resin and using them is examined.
[0003]
[Problem(s) to be Solved by the Invention] However, the organic resin into which the silyl radical was introduced is not yet enough as physical properties, such as a degree of hardness of a paint film, and chemical resistance. Moreover, what has the organic radical which linked alkoxysilane and these with silicon directly among the oligomer which carried out partial hydrolysis condensation does not have enough physical properties, such as a degree of hardness of the paint film obtained. This is considered because bridge formation is not enough. Even if it is alkoxysilane which the organic radical has combined with silicon through an oxygen atom altogether, a tetra-ethoxy silane, tetra-butoxysilane, etc. do not have [what is examined conventionally] physical properties enough [on the other hand,], such as a degree of hardness of the paint film from which all are obtained too, and chemical resistance, for example. This is considered [having come to raise extent of hydrolysis and condensation enough / sake]. Physical properties, such as a degree of hardness of the paint film from which a tetramethoxy silane is obtained among these alkoxysilane, and chemical resistance, become the outstanding thing among the alkoxysilane which the organic radical has combined with silicon through an oxygen atom altogether. However, the liquid at the time of considering as a hardenability constituent has a problem in preservation stability the top where toxicity is [that it is strong and handling is also difficult and] dangerous that it is very easy to gel. Moreover, it is difficult for there to be a problem also in compatibility with various organic components, such as resin, when it considers as oligomer for the purpose of toxic relief etc., and to even consider as a paint film.
[0004]
[Means for Solving the Problem] Then, when this invention persons inquired wholeheartedly in view of the above-mentioned technical problem, the siloxane compound expressed with a specific rational formula was excellent also in compatibility with various components, and it blends with other components, and it finds to offer the very useful hardenability constituent which can solve the above-mentioned technical problem, and dramatically excellent independent or / this siloxane compound] in the stability in the various inside of a solvent, and it came to complete this invention. Namely, this invention (1) The siloxane compound, [0005] which are expressed with the following rational formulas
[Formula 3] $SiO_a(OH)_b(OR1)_c(OR2)_d$ ($0.8 \leq a \leq 1.6$, $0.3 \leq b \leq 1.3$, $0.2 \leq c+d \leq 1.9$, $b=4-(2a+c+d)$, organic radical on which a methyl group or an ethyl group, and R2 are [R1] different from each other with R1)
(2) Siloxane compound according to claim 1 whose R1 is a methyl group (3) Hydrolysis condensation of the alkoxysilane shown by $Si(OR1)_4$ is carried out, and it is [0006].
[Formula 4]



(— the manufacture approach of a siloxane compound expressed with the above-mentioned rational formula characterized by including the process which n considers as the oligomer expressed with or more 2 eight or less integer), and adds and carries out the ester interchange of the alcohol expressed with R2OH to this and [0007] however,] (4) Consist in the hardenability constituent which comes to blend with this and a compound with compatibility the siloxane compound expressed with the above-mentioned rational formula. Hereafter, this invention is explained to a detail. First, the siloxane compound in that of this invention is expressed with the following rational formulas.
[0008]
[Formula 5] $SiO_a(OH)_b(OR1)_c(OR2)_d$ [0009] here -- $0.8 \leq a \leq 1.6$ — it is $0.85 \leq a \leq 1.4$ preferably. At the time of $a < 0.8$, the hardened material which hardens this and is obtained becomes opaque, and is not suitable for obtaining a transparence paint film. Moreover, at the time of $1.6 < a$, the viscosity of liquid is highly unstable and it is easy to gel it.

Moreover, actuation of paint-film-izing etc. may become difficult. 0.3<=b<=1.3 -- it is 0.5<=b<=0.9 preferably. In the case of b< 0.3, what paint-film-ized this is inferior to boiling water resistance. That is, if boiling is continued by ebullition underwater, the film exfoliates from a substrate in about 3 hours, or the phenomenon of disappearing is seen, and utilization is difficult. In 1.3<b, the hardened material which hardens this and is obtained may become opaque. It is the range of 0.5<=b<=0.9, and the paint film which especially transparency is high and was excellent also in boiling water resistance can be obtained.

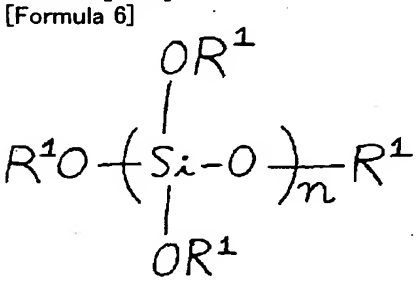
[0010] 0.2 <=c+d<=1.9 -- it is 0.2 <=c+d<=1.0 preferably. In the case of c+d<0.2, what paint-film-ized this does not have enough boiling water resistance. In 1.9<c+d, it becomes opaque, and is [make,] and the hardened material which hardens this and is obtained is **. It is 0.2 <=c+d<=1.0 and the paint film which especially transparency is high and was excellent also in boiling water resistance can be obtained.

[0011] When R2 mentioned later was an ethyl group, it shall be the range of 1.1<=a<=1.3, 0.6<=b<=0.8, and 0.7 <=c+d<=0.9, and the liquid property and the paint film property should be especially excellent. These values can choose the still more desirable range suitably also according to the class of the solvent, when the siloxane compound of this invention exists in various kinds of solvents. Moreover, what is necessary is just to choose suitably with a desired liquid property and the property of a hardened material. Furthermore, what is necessary is just to choose suitably by the component blended when blending the siloxane compound of this invention with other components and considering as a hardenability constituent, an application, the paint film approach which are used, etc.

[0012] R1 is a methyl group or an ethyl group. In the case of a methyl group, it excels in physical properties, such as a degree of hardness of a hardened material, and chemical resistance, especially. R2 is R1 and an organic radical which is different from each other. The organic radical which univalent or divalent alcohol specifically has that what is necessary is just the organic radical which can carry out an ester interchange to R1 preferably, For example, an ethyl group, an isopropyl group, butyl, a 1-methoxy-2-ethyl group, A 1-ethoxy-2-propyl group, a 1-methoxy-2-propyl group, 2-methoxy ethyl group, 2-ethoxyethyl radical, C2H5OC2H4OC2H4-, CH3C2H4OC2H4-, C2H5OC2H4-, CH3OC2H4-, etc. are mentioned.

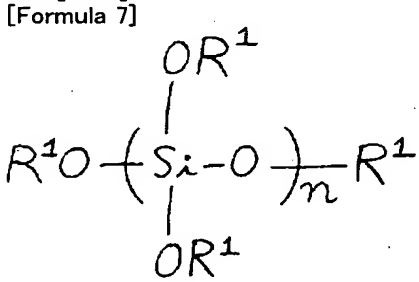
[0013] What is necessary is just to choose suitably according to the application and the object of a siloxane compound, since it is possible to control reactivity and a liquid property by the class of these organic radicals. For example, what is necessary is to blend and also just to consider as curing temperature and the thing according to the class of component etc. Generally the small organic radical of C number is in the inclination to excel in a cure rate and the degree of hardness of a hardened material, and especially when R2 is an ethyl group, it excels in these points. It may be good to introduce a specific organic radical for the object [component / combination] of compatibility adjustment depending on an application and the coating approach, on the other hand, since it is not desirable for a cure rate to be not much large. In any case, the siloxane compound of this invention expressed with the above-mentioned rational formula can be used suitably. Especially the approach for obtaining the siloxane compound of this invention can be acquired by the manufacture approach of this invention, for example, although what was not limited but was obtained by which approach corresponds. That is, hydrolysis condensation of the alkoxysilane shown by Si (OR1)4 is carried out, and it is [0014].

[Formula 6]



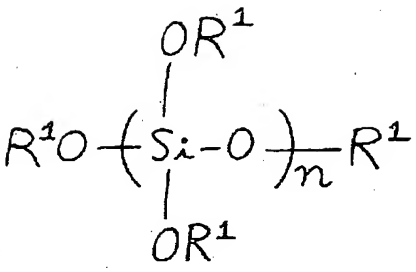
(— however, n can be obtained by the manufacture approach including the process which considers as the oligomer expressed with or more 2 eight or less integer), and adds and carries out the ester interchange of the alcohol expressed with R2OH to this. Hydrolysis condensation of the alkoxysilane shown by Si (OR1)4 is carried out here, and it is [0015].

[Formula 7]



(-- however, n is faced considering as the oligomer expressed with or more 2 eight or less integer), and can take a well-known approach. For example, it is [0016] by advancing the condensation reaction which follows hydrolysis and this while distilling off R1OH which adds the water of the specified quantity to the alkoxysilane shown by Si (OR1)4, and carries out a byproduction to the bottom of existence of an acid catalyst etc. if needed.

[Formula 8]



(— however, n becomes the oligomer expressed with or more 2 eight or less integer). Under the present circumstances, what is necessary is just to choose suitably according to the object, since n can be changed with the amount of the water to add. In addition, although the oligomer obtained in this way is the mixture of the compound with which the values of n usually differ, the following [taking the means of dissociating especially ****** and remains as it is] should just perform an ester interchange.

[0017] Next, the ester interchange of the alcohol expressed with R2OH is added and carried out to the oligomer obtained in this way. If water is made to exist in case this ester interchange is performed, since an OH radical arises in oligomer at progress and coincidence of an ester interchange and the siloxane compound of direct this invention can be obtained, it is desirable. Or what carried out the ester interchange can be hydrolyzed further, an OH radical can be given, and the siloxane compound of this invention can also be obtained.

[0018] Although it is calculable with the presentation of a desired siloxane compound, even if the addition of the alcohol expressed with R2OH here and the addition of water are excessive amounts, they do not interfere.

[0019] The siloxane compound of this invention can be obtained also by making the alcohol and water which are expressed with R2OH exist, in case what was beforehand made into oligomer in this way is depended on the manufacture approach which carries out an ester interchange and also hydrolysis condensation of the alkoxysilane shown by Si (OR1)4 is carried out. In addition, what is necessary is just to advance the alkoxysilane in the inside of the solvent which does not carry out an ester interchange, and/or hydrolysis of the oligomer as a siloxane compound of this invention, to extent which obtains the siloxane compound of this invention, in order to obtain the thing of d= 0.

[0020] Thus, the siloxane compound of this invention which can be obtained is excellent in compatibility with various kinds of organic components and a mineral constituent. here — compatibility — the shape of an appearance — it becomes 1 uniform liquid, the condition that the activity of spreading to a substrate etc. can be presented is said, and it is not necessarily restricted to what the siloxane compound is dissolving thoroughly, but the condition of distributing as colloid and an emulsion is also included.

[0021] Therefore, the siloxane compound of this invention can be blended with a compound with this and compatibility, i.e., organic [various kinds of], and a mineral constituent, and can be used as a useful hardenability constituent. If it blends with various kinds of resinous principles and organic compounds, such as a silane coupler, especially, organic–inorganic hybrid constituent can be obtained easily and it is very useful. For example, it is suitable also for surface treatment, such as spreading to a base material, impregnation, and fine particles, a granular object. Of course, the siloxane compound of this invention can also be independently used as a hardenability constituent, and room temperature setting can also obtain the glassiness of a high degree of hardness. Since the siloxane compound of this invention can stop the viscosity of rear–spring–supporter liquid low at a long period of time, when it uses for a paint film–ized application independently, it can make thickness very uniform and is suitable also for the application of a spin coat etc. In addition, to these hardenability constituent, a well–known catalyst component can be added if needed, and hardening can also be promoted.

[0022]

[Example] Hereafter, an example explains this invention to a detail further.

The tetramethoxy silane (shown by Si (OCH3)4) 117 weight section was dissolved in the example 1 methanol 37 weight section, after heating 65 degrees C of things which added the hydrochloric–acid 11.1 weight section 0.05% for 2 hours and advancing a hydrolysis condensation reaction, temperature up was carried out further and the methanol and the unreacted tetramethoxy silane were removed. The oligomer of polymerization degree 2–8 was checked by GPC analysis. When the rational formula was searched for with the amount of generation methanols measured with the charge and gas chromatography of water, all obtained SiO0.8 (OCH3) 2.4.

[0023] In this way, to the obtained oligomer 30.77 weight section, under the room temperature, what added the ethanol 62.4 weight section, the maleic–acid 0.308 weight section, and the water 6.519 weight section was stirred until it became the liquefied object of transparent homogeneity.

[0024] The rational formula of the siloxane compound in this liquefied object was searched for by the following approaches.

(1) Ask for the number of O atoms combined with Si atom by 29 Si–NMR, and calculate the value of a multiplier a in the following rational formula (A).

(2) Calculate the value of multipliers c and d in the following rational formula (A) from the integral ratio of three peaks, the methanol in the chart of 13 C–NMR, a methoxy group, and an ethoxy radical. (It calculated considering the premise of a reaction as the following passages.)

[0025]

[Formula 9]

$$SiO_{0.8}(OCH_3)_{2.4} + H_2O/H^+_3O + R^2OH$$

$$\rightleftarrows SiO_a(OH)_b(OCH_3)_c(OR^2)_d + (2.4-c)CH_3OH$$

$$^{13}C: \frac{Int(CH_3OH)}{Int(CH_3O\text{-}Si)} = \frac{2.4-c}{c}$$

$$^{13}C: \frac{Int(R^2O\text{-}Si)}{Int(CH_3O\text{-}Si)} = \frac{d}{c}$$

[0026] (3) Calculate the value of b in the following rational formula (A) from b=4- (2 a+c+d).
SiOa(OH)b(OCH3) c(OC2H5) d ..... (A)
Aging of a-d in the rational formula of a siloxane compound is shown in a table 1.
[0027]
[A table 1]

表1

	3時間後	6時間後	1日後	3日後	8日後	15日後	31日後
a	0.84	0.89	1.06	1.24	1.3	1.44	1.51
b	1.1	1.02	1.04	0.65	0.64	0.57	0.42
c	0.49	0.42	0.3	0.29	0.31	0.17	0.19
d	0.73	0.78	0.54	0.58	0.39	0.38	0.41
c+d	1.22	1.20	0.84	0.87	0.70	0.55	0.60

[0028] It replaced with two to example 5 ethanol, and the same actuation as an example 1 was performed except having used propylene glycol monomethyl ether, the propylene glycol monoethyl ether, the acetone, and the tetrahydrofuran respectively. Aging of a-d in the rational formula of the siloxane compound obtained by the same approach is shown in tables 2-5.
[0029]
[A table 2]

表2

	3時間後	6時間後	3日後	8日後
a	0.81	0.85	1.12	1.27
b	1.19	1.2	0.91	0.71
c	0.96	0.85	0.59	0.56
d	0.23	0.25	0.26	0.19
c+d	1.19	1.10	0.85	0.75

[0030]
[A table 3]

表3

	3時間後	6時間後	3日後	8日後
a	0.83	0.88	1.19	1.28
b	1.13	1.04	0.75	0.66
c	0.99	0.85	0.6	0.53
d	0.22	0.35	0.27	0.25
c+d	1.21	1.20	0.87	0.78

[0031]
[A table 4]
表4

	1日後	8日後	15日後	31日後
a	1.21	1.36	1.43	1.5
b	0.92	0.83	0.73	0.55
c	0.66	0.45	0.41	0.45
d	—	—	—	—
c+d	0.66	0.45	0.41	0.45

[0032]
[A table 5]
表5

	1日後	8日後	15日後
a	0.91	1.21	1.31
b	1.4	0.95	0.82
c	0.78	0.63	0.56
d	—	—	—
c+d	0.78	0.63	0.56

[0033] The time amount after preparation of the liquefied object obtained in the example 6 example 1, the appearance of the paint film obtained by carrying out heat hardening at a pull-up and 150 degrees C in a second in 3mm /for 1 hour after the glass substrate was immersed in this liquefied object, and boiling water resistance (appearance of the film after boiling by ebullition underwater the whole substrate for 3 hours) are shown in a table 6. The pencil degree of hardness of these paint films (based on JIS K5651.) It is below the same. Each was 9H. About the liquid three days after after preparation, and of five days after, it replaced with 150-degree C 1-hour heat hardening, and except having left it on the 6th and having hardened under the room temperature, when the above-mentioned actuation and same actuation were performed, the paint film even with after [transparent] a boiling water resistance test was obtained by appearance transparence and pencil degree-of-hardness 9H.
[0034]
[A table 6]

表6

	3時間後	6時間後	3日後	5日後	31日後
加熱硬化後の膜外観	透明	透明	透明	透明	透明
耐沸水性試験後の膜外観	微白	微白	透明	透明	膜消失

[0035] After preparation of the liquefied object obtained in the example 7 example 1, when the liquid 81 weight section on the 3rd was mixed with the silane coupler ("KBM-1003" by Shin-Etsu Chemical Co., Ltd. shown by chemical formula CH2=CHSi (OCH3)3) 17 weight section, it could consider as the liquefied object of homogeneity and excelled in compatibility. The pencil degree of hardness of the transparent paint film obtained by performing pull-up of the substrate by the same actuation as an example 6 and 150-degree C 1-hour heat hardening was 9H. Moreover, even after dropping the sulfuric acid 5% and passing through 24 hours, change was not looked at by the appearance of a paint film, but was excellent in it at chemical resistance.

[0036] After preparation of the liquefied object obtained in the example 8 example 1, when the liquid 46 weight section on the 3rd was mixed with the hydroxy group content acrylic resin 53 weight section, it could consider as the liquefied object of homogeneity and excelled in compatibility. After leaving it after mixing this for 12 hours, when it applied to the substrate and heat hardening was carried out at 150 degrees C for 2 hours, the transparent paint film was able to be obtained.

The same actuation as an example 1 was performed except having used aluminum acetylacetonate instead of the example 9 maleic acid. The value of a-d calculated by the same approach and c+d is shown in a table 7.

[0037]

[A table 7]

表7

	1日後	3日後	8日後
a	0.84	1.15	1.32
b	0.95	0.68	0.55
c	0.81	0.37	0.26
d	0.56	0.65	0.55
c+d	1.37	1.02	0.81

[0038] When a-d and c+d immediately after preparation of the liquefied object obtained in the example of comparison 1 example 1 were calculated by the same approach as an example 1, it is a= 0.8, b= 0, c= 2.4, and d= 0. It was thereforec+d=2.4. When this liquefied object was paint-film-ized by heat hardening by the same approach as an example 6 for 150-degree-C 1 hour, the appearance of a paint film was milked.

[0039] The spin coat was carried out by 3000rpm using the liquid on the 8th immediately after preparation of the liquefied object obtained in the example 9 example 1. The thickness average after BEKU is 4020A at 400 degrees C, and thickness homogeneity was excellent in **1.4% and homogeneity.

[0040] It was a= 1.7 when the value of a was calculated by the same approach as an example 1 using the liquid 60 days after [of the liquefied object obtained in the example of comparison 2 example 1] immediately after preparation. Viscosity is high, the fluidity of liquid was low, and, as for the film obtained by the same approach as an example 9, 4900A and thickness homogeneity were inferior to **4.2% and homogeneity in the thickness average.

[0041]

[Effect of the Invention] It excels in compatibility with various components, and the stability in the various inside of a solvent, and independent or the new siloxane compound which can blend with other components and can offer a very useful hardenability constituent is obtained.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to a hardenability constituent at a siloxane compound and its manufacture approach, and a list.

[Translation done.]

PRIOR ART

[Description of the Prior Art] By introducing a silyl radical into organic resin, the improvement of the degree of hardness of a paint film, acid resistance, etc. is tried conventionally. Furthermore, alkoxysilane, such as a tetra-ethoxy silane, a tetramethoxy silane, methyl trimetoxysilane, ethyltrimethoxysilane, dimethyldimethoxysilane, and vinyltrimetoxysilane, and the oligomer which carried out partial hydrolysis condensation of these are independently used as a coating agent in recent years, or blending these with resin and using them is examined.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] It excels in compatibility with various components, and the stability in the various inside of a solvent, and independent or the new siloxane compound which can blend with other components and can offer a very useful hardenability constituent is obtained.

[Translation done.]

TECHNICAL PROBLEM

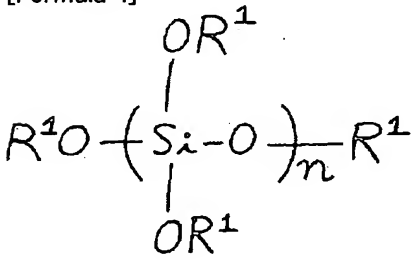
[Problem(s) to be Solved by the Invention] However, the organic resin into which the silyl radical was introduced is not yet enough as physical properties, such as a degree of hardness of a paint film, and chemical resistance. Moreover, what has the organic radical which linked alkoxysilane and these with silicon directly among the oligomer which carried out partial hydrolysis condensation does not have enough physical properties, such as a degree of hardness of the paint film obtained. This is considered because bridge formation is not enough. Even if it is alkoxysilane which the organic radical has combined with silicon through an oxygen atom altogether, a tetra-ethoxy silane, tetra-butoxysilane, etc. do not have [what is examined conventionally] physical properties enough [on the other hand,], such as a degree of hardness of the paint film from which all are obtained too, and chemical resistance, for example. This is considered [having come to raise extent of hydrolysis and condensation enough / sake]. Physical properties, such as a degree of hardness of the paint film from which a tetramethoxy silane is obtained among these alkoxysilane, and chemical resistance, become the outstanding thing among the alkoxysilane which the organic radical has combined with silicon through an oxygen atom altogether. However, the liquid at the time of considering as a hardenability constituent has a problem in preservation stability the top where toxicity is [that it is strong and handling is also difficult and] dangerous that it is very easy to gel. Moreover, it is difficult for there to be a problem also in compatibility with various organic components, such as resin, when it considers as oligomer for the purpose of toxic relief etc., and to even consider as a paint film.

[Translation done.]

* NOTICES *

MEANS

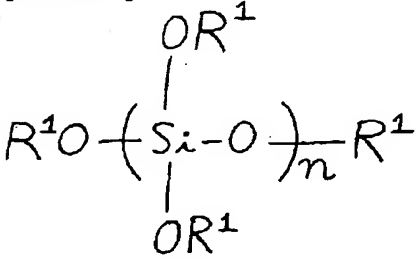
[Means for Solving the Problem] Then, when this invention persons inquired wholeheartedly in view of the above-mentioned technical problem, the siloxane compound expressed with a specific rational formula was excellent also in compatibility with various components, and it blends with other components, and it finds to offer the very useful hardenability constituent which can solve the above-mentioned technical problem, and dramatically excellent independent or / this siloxane compound] in the stability in the various inside of a solvent, and it came to complete this invention. Namely, this invention (1) The siloxane compound, [0005] which are expressed with the following rational formulas
[Formula 3] SiOa(OH)b(OR1) c(OR2) d (0.8<=a<=1.6, 0.3<=b<=1.3, 0.2 <=c+d<=1.9, b=4- (2 a+c+d), organic radical on which a methyl group or an ethyl group, and R2 are [R1] different from each other with R1)
(2) Siloxane compound according to claim 1 whose R1 is a methyl group (3) Hydrolysis condensation of the alkoxysilane shown by Si (OR1)4 is carried out, and it is [0006].
[Formula 4]



(— the manufacture approach of a siloxane compound expressed with the above-mentioned rational formula characterized by including the process which n considers as the oligomer expressed with or more 2 eight or less integer), and adds and carries out the ester interchange of the alcohol expressed with R2OH to this and [0007] however,] (4) Consist in the hardenability constituent which comes to blend with this and a compound with compatibility the siloxane compound expressed with the above-mentioned rational formula. Hereafter, this invention is explained to a detail. First, the siloxane compound in that of this invention is expressed with the following rational formulas.
[0008]
[Formula 5] SiOa(OH)b(OR1) c(OR2) d [0009] here — 0.8<=a<=1.6 — it is 0.85<=a<=1.4 preferably. At the time of a< 0.8, the hardened material which hardens this and is obtained becomes opaque, and is not suitable for obtaining a transparence paint film. Moreover, at the time of 1.6<a, the viscosity of liquid is highly unstable and it is easy to gel it. Moreover, actuation of paint-film-izing etc. may become difficult. 0.3<=b<=1.3 — it is 0.5<=b<=0.9 preferably. In the case of b< 0.3, what paint-film-ized this is inferior to boiling water resistance. That is, if boiling is continued by ebullition underwater, the film exfoliates from a substrate in about 3 hours, or the phenomenon of disappearing is seen, and utilization is difficult. In 1.3<b, the hardened material which hardens this and is obtained may become opaque. It is the range of 0.5<=b<=0.9, and the paint film which especially transparency is high and was excellent also in boiling water resistance can be obtained.
[0010] 0.2 <=c+d<=1.9 — it is 0.2 <=c+d<=1.0 preferably. In the case of c+d<0.2, what paint-film-ized this does not have enough boiling water resistance. In 1.9<c+d, it becomes opaque, and is [make,] and the hardened material which hardens this and is obtained is **. It is 0.2 <=c+d<=1.0 and the paint film which especially transparency is high and was excellent also in boiling water resistance can be obtained.
[0011] When R2 mentioned later was an ethyl group, it shall be the range of 1.1<=a<=1.3, 0.6<=b<=0.8, and 0.7 <=c+d<=0.9, and the liquid property and the paint film property should be especially excellent. These values can choose the still more desirable range suitably also according to the class of the solvent, when the siloxane compound of this invention exists in various kinds of solvents. Moreover, what is necessary is just to choose suitably with a desired liquid property and the property of a hardened material. Furthermore, what is necessary is just to choose suitably by the component blended when blending the siloxane compound of this invention with other components and considering as a hardenability constituent, an application, the paint film approach which are used, etc.
[0012] R1 is a methyl group or an ethyl group. In the case of a methyl group, it excels in physical properties, such as a degree of hardness of a hardened material, and chemical resistance, especially. R2 is R1 and an organic radical which is different from each other. The organic radical which univalent or divalent alcohol specifically has that what is necessary is just the organic radical which can carry out an ester interchange to R1 preferably, For example, an ethyl group, an isopropyl group, butyl, a 1-methoxy-2-ethyl group, A 1-ethoxy-2-propyl group, a 1-methoxy-2-propyl group, 2-methoxy ethyl group, 2-ethoxyethyl radical, C2H5OC2H4OC2H4-, CH3C2H4OC2H4-, C2H5OC2H4-, CH3OC2H4-, etc. are mentioned.
[0013] What is necessary is just to choose suitably according to the application and the object of a siloxane compound, since it is possible to control reactivity and a liquid property by the class of these organic radicals. For example, what is necessary is to blend and also just to consider as curing temperature and the thing according to the class of component etc. Generally the small organic radical of C number is in the inclination to excel in a cure rate and the

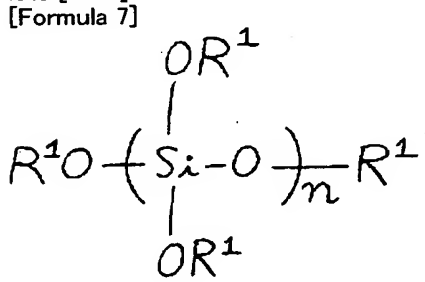
degree of hardness of a hardened material, and especially when R2 is an ethyl group, it excels in these points. It may be good to introduce a specific organic radical for the object [component / combination] of compatibility adjustment depending on an application and the coating approach, on the other hand, since it is not desirable for a cure rate to be not much large. In any case, the siloxane compound of this invention expressed with the above-mentioned rational formula can be used suitably. Especially the approach for obtaining the siloxane compound of this invention can be acquired by the manufacture approach of this invention, for example, although what was not limited but was obtained by which approach corresponds. That is, hydrolysis condensation of the alkoxysilane shown by Si (OR1)4 is carried out, and it is [0014].

[Formula 6]



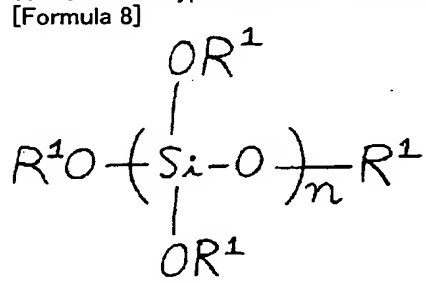
(-- however, n can be obtained by the manufacture approach including the process which considers as the oligomer expressed with or more 2 eight or less integer), and adds and carries out the ester interchange of the alcohol expressed with R2OH to this. Hydrolysis condensation of the alkoxysilane shown by Si (OR1)4 is carried out here, and it is [0015].

[Formula 7]



(-- however, n is faced considering as the oligomer expressed with or more 2 eight or less integer), and can take a well-known approach. For example, it is [0016] by advancing the condensation reaction which follows hydrolysis and this while distilling off R1OH which adds the water of the specified quantity to the alkoxysilane shown by Si (OR1)4, and carries out a byproduction to the bottom of existence of an acid catalyst etc. if needed.

[Formula 8]



(-- however, n becomes the oligomer expressed with or more 2 eight or less integer). Under the present circumstances, what is necessary is just to choose suitably according to the object, since n can be changed with the amount of the water to add. In addition, although the oligomer obtained in this way is the mixture of the compound with which the values of n usually differ, the following [taking the means of dissociating especially ****** and remains as it is] should just perform an ester interchange.

[0017] Next, the ester interchange of the alcohol expressed with R2OH is added and carried out to the oligomer obtained in this way. If water is made to exist in case this ester interchange is performed, since an OH radical arises in oligomer at progress and coincidence of an ester interchange and the siloxane compound of direct this invention can be obtained, it is desirable. Or what carried out the ester interchange can be hydrolyzed further, an OH radical can be given, and the siloxane compound of this invention can also be obtained.

[0018] Although it is calculable with the presentation of a desired siloxane compound, even if the addition of the alcohol expressed with R2OH here and the addition of water are excessive amounts, they do not interfere.

[0019] The siloxane compound of this invention can be obtained also by making the alcohol and water which are expressed with R2OH exist, in case what was beforehand made into oligomer in this way is depended on the manufacture approach which carries out an ester interchange and also hydrolysis condensation of the alkoxysilane shown by Si (OR1)4 is carried out. In addition, what is necessary is just to advance the alkoxysilane in the inside of the solvent which does not carry out an ester interchange, and/or hydrolysis of the oligomer as a siloxane compound of this invention, to extent which obtains the siloxane compound of this invention, in order to obtain the thing of d= 0.

[0020] Thus, the siloxane compound of this invention which can be obtained is excellent in compatibility with various kinds of organic components and a mineral constituent. here -- compatibility -- the shape of an appearance -- it becomes 1 uniform liquid, the condition that the activity of spreading to a substrate etc. can be presented is said, and it is not necessarily restricted to what the siloxane compound is dissolving thoroughly, but the condition of distributing

as colloid and an emulsion is also included.
[0021] Therefore, the siloxane compound of this invention can be blended with a compound with this and compatibility, i.e., organic [various kinds of], and a mineral constituent, and can be used as a useful hardenability constituent. If it blends with various kinds of resinous principles and organic compounds, such as a silane coupler, especially, organic-inorganic hybrid constituent can be obtained easily and it is very useful. For example, it is suitable also for surface treatment, such as spreading to a base material, impregnation, and fine particles, a granular object. Of course, the siloxane compound of this invention can also be independently used as a hardenability constituent, and room temperature setting can also obtain the glassiness of a high degree of hardness. Since the siloxane compound of this invention can stop the viscosity of rear-spring-supporter liquid low at a long period of time, when it uses for a paint film-ized application independently, it can make thickness very uniform and is suitable also for the application of a spin coat etc. In addition, to these hardenability constituent, a well-known catalyst component can be added if needed, and hardening can also be promoted.

[Translation done.]

EXAMPLE

[Example] Hereafter, an example explains this invention to a detail further.
The tetramethoxy silane (shown by Si (OCH3)4) 117 weight section was dissolved in the example 1 methanol 37 weight section, after heating 65 degrees C of things which added the hydrochloric-acid 11.1 weight section 0.05% for 2 hours and advancing a hydrolysis condensation reaction, temperature up was carried out further and the methanol and the unreacted tetramethoxy silane were removed. The oligomer of polymerization degree 2-8 was checked by GPC analysis. When the rational formula was searched for with the amount of generation methanols measured with the charge and gas chromatography of water, all obtained SiO0.8 (OCH3) 2.4.
[0023] In this way, to the obtained oligomer 30.77 weight section, under the room temperature, what added the ethanol 62.4 weight section, the maleic-acid 0.308 weight section, and the water 6.519 weight section was stirred until it became the liquefied object of transparent homogeneity.
[0024] The rational formula of the siloxane compound in this liquefied object was searched for by the following approaches.
(1) Ask for the number of O atoms combined with Si atom by 29 Si-NMR, and calculate the value of a multiplier a in the following rational formula (A).
(2) Calculate the value of multipliers c and d in the following rational formula (A) from the integral ratio of three peaks, the methanol in the chart of 13 C-NMR, a methoxy group, and an ethoxy radical. (It calculated considering the premise of a reaction as the following passages.)
[0025]
[Formula 9]

$$SiO_{0.8}(OCH_3)_{2.4} + H_2O/H^+_3O + R^2OH$$

$$\rightleftarrows SiO_a(OH)_b(OCH_3)_c(OR^2)_d + (2.4-c)CH_3OH$$

$$^{13}C: \frac{Int(CH_3OH)}{Int(CH_3O\text{-}Si)} = \frac{2.4-c}{c}$$

$$^{13}C: \frac{Int(R^2O\text{-}Si)}{Int(CH_3O\text{-}Si)} = \frac{d}{c}$$

[0026] (3) Calculate the value of b in the following rational formula (A) from b=4- (2 a+c+d).
SiOa(OH)b(OCH3) c(OC2H5) d ..... (A)
Aging of a-d in the rational formula of a siloxane compound is shown in a table 1.
[0027]
[A table 1]

表1

	3時間後	6時間後	1日後	3日後	8日後	15日後	31日後
a	0.84	0.89	1.06	1.24	1.3	1.44	1.51
b	1.1	1.02	1.04	0.65	0.64	0.57	0.42
c	0.49	0.42	0.3	0.29	0.31	0.17	0.19
d	0.73	0.78	0.54	0.58	0.39	0.38	0.41
c+d	1.22	1.20	0.84	0.87	0.70	0.55	0.60

[0028] It replaced with two to example 5 ethanol, and the same actuation as an example 1 was performed except having used propylene glycol monomethyl ether, the propylene glycol monoethyl ether, the acetone, and the tetrahydrofuran respectively. Aging of a-d in the rational formula of the siloxane compound obtained by the same approach is shown in tables 2-5.
[0029]
[A table 2]

表2

	3時間後	6時間後	3日後	8日後
a	0.81	0.85	1.12	1.27
b	1.19	1.2	0.91	0.71
c	0.96	0.85	0.59	0.56
d	0.23	0.25	0.26	0.19
c+d	1.19	1.10	0.85	0.75

[0030]
[A table 3]
表3

	3時間後	6時間後	3日後	8日後
a	0.83	0.88	1.19	1.28
b	1.13	1.04	0.75	0.66
c	0.99	0.85	0.6	0.53
d	0.22	0.35	0.27	0.25
c+d	1.21	1.20	0.87	0.78

[0031]
[A table 4]
表4

	1日後	8日後	15日後	31日後
a	1.21	1.36	1.43	1.5
b	0.92	0.83	0.73	0.55
c	0.66	0.45	0.41	0.45
d	—	—	—	—
c+d	0.66	0.45	0.41	0.45

[0032]
[A table 5]
表5

	1日後	8日後	15日後
a	0.91	1.21	1.31
b	1.4	0.95	0.82
c	0.78	0.63	0.56
d	—	—	—
c+d	0.78	0.63	0.56

[0033] The time amount after preparation of the liquefied object obtained in the example 6 example 1, the appearance of the paint film obtained by carrying out heat hardening at a pull-up and 150 degrees C in a second in 3mm /for 1 hour after the glass substrate was immersed in this liquefied object, and boiling water resistance (appearance of the film

after boiling by ebullition underwater the whole substrate for 3 hours) are shown in a table 6. The pencil degree of hardness of these paint films (based on JIS K5651.) It is below the same. Each was 9H. About the liquid three days after after preparation, and of five days after, it replaced with 150-degree C 1-hour heat hardening, and except having left it on the 6th and having hardened under the room temperature, when the above-mentioned actuation and same actuation were performed, the paint film even with after [transparent] a boiling water resistance test was obtained by appearance transparence and pencil degree-of-hardness 9H.

[0034]

[A table 6]

表6

	3時間後	6時間後	3日後	5日後	31日後
加熱硬化後の膜外観	透明	透明	透明	透明	透明
耐沸水性試験後の膜外観	微白	微白	透明	透明	膜消失

[0035] After preparation of the liquefied object obtained in the example 7 example 1, when the liquid 81 weight section on the 3rd was mixed with the silane coupler ("KBM-1003" by Shin-Etsu Chemical Co., Ltd. shown by chemical formula CH2=CHSi (OCH3)3) 17 weight section, it could consider as the liquefied object of homogeneity and excelled in compatibility. The pencil degree of hardness of the transparent paint film obtained by performing pull-up of the substrate by the same actuation as an example 6 and 150-degree C 1-hour heat hardening was 9H. Moreover, even after dropping the sulfuric acid 5% and passing through 24 hours, change was not looked at by the appearance of a paint film, but was excellent in it at chemical resistance.

[0036] After preparation of the liquefied object obtained in the example 8 example 1, when the liquid 46 weight section on the 3rd was mixed with the hydroxy group content acrylic resin 53 weight section, it could consider as the liquefied object of homogeneity and excelled in compatibility. After leaving it after mixing this for 12 hours, when it applied to the substrate and heat hardening was carried out at 150 degrees C for 2 hours, the transparent paint film was able to be obtained.

The same actuation as an example 1 was performed except having used aluminum acetylacetonate instead of the example 9 maleic acid. The value of a-d calculated by the same approach and c+d is shown in a table 7.

[0037]

[A table 7]

表7

	1日後	3日後	8日後
a	0.84	1.15	1.32
b	0.95	0.68	0.55
c	0.81	0.37	0.26
d	0.56	0.65	0.55
c+d	1.37	1.02	0.81

[0038] When a-d and c+d immediately after preparation of the liquefied object obtained in the example of comparison 1 example 1 were calculated by the same approach as an example 1, it is a= 0.8, b= 0, c= 2.4, and d= 0. It was therefore c+d=2.4. When this liquefied object was paint-film-ized by heat hardening by the same approach as an example 6 for 150-degree-C 1 hour, the appearance of a paint film was milked.

[0039] The spin coat was carried out by 3000rpm using the liquid on the 8th immediately after preparation of the liquefied object obtained in the example 9 example 1. The thickness average after BEKU is 4020A at 400 degrees C, and thickness homogeneity was excellent in **1.4% and homogeneity.

[0040] It was a= 1.7 when the value of a was calculated by the same approach as an example 1 using the liquid 60 days after [of the liquefied object obtained in the example of comparison 2 example 1] immediately after preparation. Viscosity is high, the fluidity of liquid was low, and, as for the film obtained by the same approach as an example 9, 4900A and thickness homogeneity were inferior to **4.2% and homogeneity in the thickness average.

[0041]

[Translation done.]